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Thermal and catalytic pyrolysis of Karanja seed to produce liquid fuel

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HIGHLIGHTS

- 55.17%, Weight basis yield was reported for thermal pyrolysis of Karanja seed.
- CaO, Al_2O_3 and Kaolin were used as catalysts for catalytic pyrolysis.
- The yield of pyrolytic oil was high at 8:1 feed to catalyst ratio.
- Al_2O_3 and Kaolin proved to be better than CaO in terms of pyrolytic liquid yield.
- All the catalysts were capable to enhance the fuel quality of pyrolytic oil.

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ABSTRACT

Thermal and catalytic pyrolysis of one non-edible oil seed Karanja was reported in this work. Thermal pyrolysis of Karanja seed was performed in a semi batch reactor at different temperatures in order to find out the optimum temperature (550 °C) for utmost liquid yield (55.17%, weight basis). The pyrolytic liquid was separated as oil and aqueous layer with a yield of 33% and 22.17% by weight respectively. The oil was rich in hydrocarbon and thus termed as pyrolytic oil which can be used as fuel. Catalytic pyrolysis was carried out at 550 °C with an aim to enhance the yield and physical properties of the pyrolytic oil. Three catalysts such as CaO, Al_2O_3 and Kaolin were used at various feed to catalytic ratios (2:1, 4:1, 8:1). Catalytic pyrolysis confirmed that lower feed to catalyst ratio (8:1) increased the yield. In terms of pyrolytic oil yield, the catalysts Al_2O_3 and Kaolin proved to be better than CaO whereas all the catalysts resulted in better quality of pyrolytic oil in comparison with thermal pyrolysis. The yield of oil was 31.28%, 34.49% and 35.17% for CaO, Al_2O_3 and Kaolin respectively. The composition analysis provided the evidence that the acids produced during thermal pyrolysis of Karanja seed got converted to esters during catalytic pyrolysis which might be the reason for the changed pH and increased calorific value.

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1. Introduction

Biomass is one of the major sources which may offer a great potential for the production of energy in the near future. Biomass can be used to produce solid, liquid as well as gaseous fuels. In the past few years, biomass derived liquid fuels such as bio-diesel, bio-ethanol, bio-butanol and bio-oil have been examined as alternative source of energy. Negligible amount of sulfur content in biomass makes it suitable as a feed stock for the production of energy. The CO_2 produced by burning of such fuels is reused by the plant itself for its growth and does not increase the fixed carbon content of the environment. Hence these fuels are considered as CO_2 neutral fuels.

Conversion of biomass to fuel may occur by biochemical and thermochemical routes. Out of these two processes, thermal conversion method is convenient and easy which requires less capital for the production of fuel. Thermochemical process is also known as pyrolysis. The oil produced by this process is called as pyrolytic oil or bio-oil. It can be used as it is or after up-gradation as a fuel for combustion engine. The conversion of biomass to pyrolytic oil may take place with or without the presence of catalyst. Literatures revealed that use of catalyst increases the fuel properties such as calorific value and decreases the viscosity of the fuel [1–3]. The yield of liquid is also a function of temperature, heating rate, catalyst type and the reactor used. Therefore at different catalytic conditions and temperature the fuel properties and compositions are different. In some cases, catalyst increases the product yield as well as the quality of pyrolytic oil. The quality and composition of the pyrolytic oils depend on the biomass composition and its extractive content. It was reported that biomass with higher amount of extractives and cellulose resulted in higher yield of liquid during pyrolysis [4]. Literatures revealed that some agricultural residues produced pyrolytic oil which can be easily separated into two phases; the top phase is organic rich and can be used as fuel whereas the bottom phase is more aqueous and can be utilized

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Table 1
Proximate and ultimate analysis of Karanja seed.

Proximate analysis	Wt. (%)	Ultimate analysis	Wt. (%)
Moisture content	7.27	Carbon (C)	53.04
Volatile matter	89.23	Hydrogen (H)	7.32
Ash content	1.5	Nitrogen (N)	3.94
Fixed carbon	2.0	Oxygen (O)	35.527
		Sulfur (S)	0.173
Extractive content			
Hexane extractives	52.74 (%)	Ethanol extractives	0.45 (%)

for production of bio-chemicals [5,6]. Apart from agricultural residues, biomass having higher extractives content produced similar types of pyrolytic oil. Top phase pyrolytic oil provides similar fuel properties such as calorific value and density as diesel whereas because of its low pH and high viscosity, it cannot be used directly as fuel for diesel engine [7]. These are the major disadvantages of pyrolytic oil. Another drawback is the pour point. Pyrolytic oil loses its flowing behavior and becomes wax at +11 °C. This creates a problem during the winter season. Hence, different cracking processes have been utilized to meet the fuel quality. Catalytic pyrolysis is one which can increase the yield of liquid as well as the quality of pyrolytic oil. It was reported that pyrolytic oil having higher oxygen content reduces the storage stability [8]. Complete deoxygenating of bio-oil can meet the fuel properties of transportation fuel such as diesel and petrol. Literatures disclosed that catalyst with silica and alumina composition and oxides of metal increased the yield and fuel properties by decreasing oxygen content of the pyrolytic oil [9–11].

In the present study, the oxides of aluminum, calcium and Kaolin were used as catalyst to study their effect on pyrolysis of Karanja seed. Literatures reported that metal oxide has a significant effect on pyrolysis to increase the physical properties and also act as a hydrodesulphurizing agent for the treatment of gasoline [12,13]. Calcium oxide (CaO) reduces the tar yield as well as emission of CO_2. CO_2 gets absorbed by CaO and forms $CaCO_3$ and hence it results in zero emission during pyrolysis [14,15]. The major composition of Kaolin is silica and alumina with little amount of zinc and other inorganic compounds and mineral components such as quartz, illites, smectites, and feldspars. Aluminum silicates are widely used in catalytic processes, such as the cracking of petroleum fractions, and elucidation of their structures and surface properties [16]. It is an inexpensive catalyst and easily available and hence preferred as a catalyst for pyrolysis [17].

In this present investigation, one non-edible oil seed Karanja (*Pongamia pinnata*) was taken as a feed for pyrolysis. Karanja seed is available in plenty in various regions of India and contains 30–40% oil by weight. Karanja oil is traditionally used for lighting of lamp and some literatures reported the production of biodiesel from this oil also. The details about the seed production, availability, and soil and climate conditions for the growth of plant are reported in the literature elsewhere [18]. The aim of the study is to improve the fuel properties of pyrolytic oil with the use of catalyst such as Al_2O_3, Kaolin and CaO during pyrolysis and to find out the optimum thermal and catalytic condition for maximum yield of pyrolytic oil from Karanja seed.

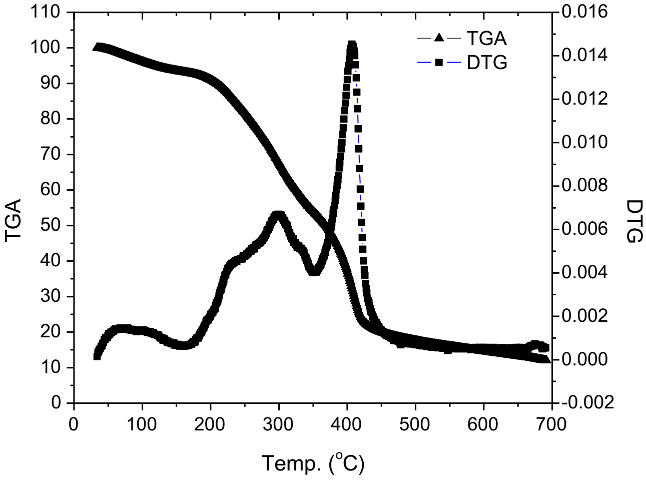

Fig. 1. TGA/DTG thermogram of Karanja seed.

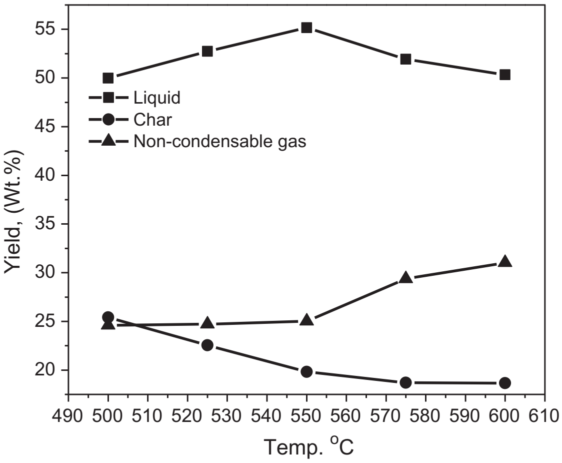

Fig. 2. Influence of temperature on pyrolysis products yield.

2. Materials and methods

2.1. Raw material

Fresh Karanja seed (*P. pinnata*) was collected from local market of Ganjam, Odisha, India. The seed materials were sundried for 10–12 h to remove maximum moisture content. Before using as feed for pyrolysis the seeds were powdered to less than 1 mm mesh size.

2.2. Characterization of raw material

Karanja seeds were characterized for their suitability as a feed for pyrolysis. The basic properties which play a significant role on the pyrolytic product composition were determined by proximate analysis followed by ASTM D 3173-3187, ASTM D 3175-89 and NREL/TP-510-42622 for moisture, volatile and ash content respectively [19–21]. The ultimate analysis which visualizes the

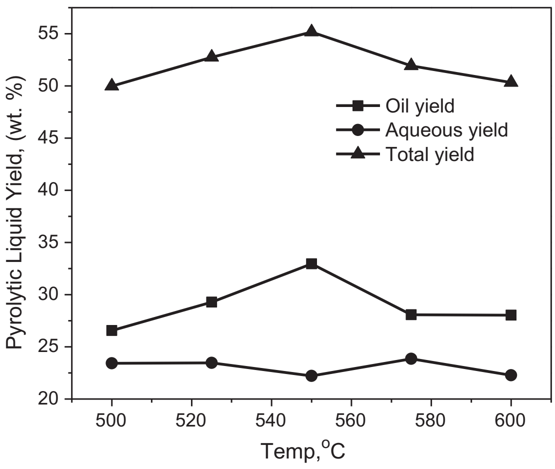

Fig. 3. Weight% yield of oil and aqueous phase pyrolytic yield.

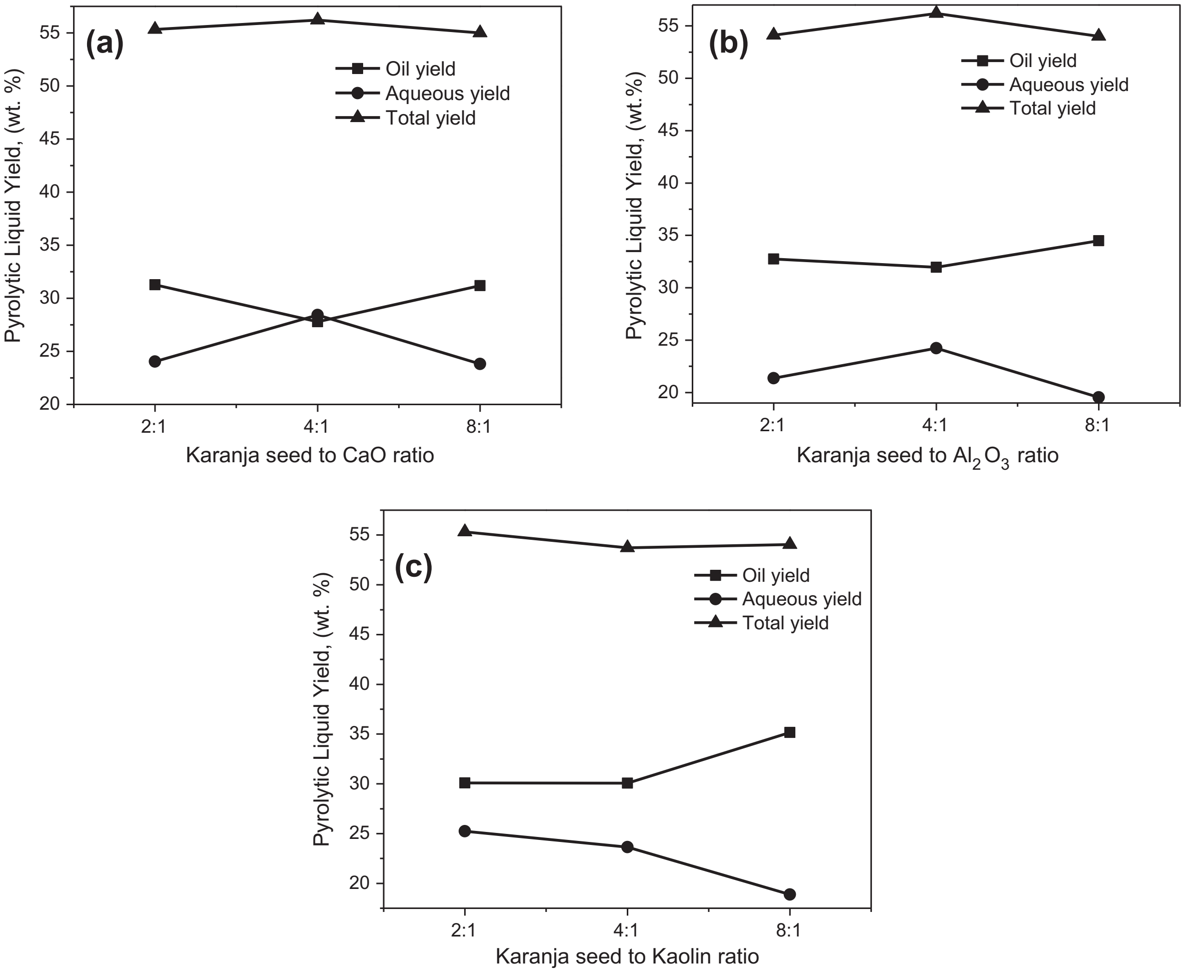

Fig. 4. Effect of catalyst (a) CaO, (b) Al_2O_3 and (c) Kaolin on pyrolytic liquid yield.

presence of C, H, N, S and O was determined by Germany made Variael CUBE C, H, N, S elemental analyzer. The oxygen content was calculated by difference. In general, seed materials embrace maximum oil or extractives other than cellulose, hemicelluloses and lignin. To calculate extractives content of Karanja seed the powdered seed samples were treated with ethanol followed by hexane with the help Soxhlet apparatus and thimble followed by NREL/TP-510-42619 standard methods [18,22]. Thermogravimetric (TG) analysis of Karanja seed was carried out from 25 to 700 °C at a heating rate of 20 °C min^{-1} under N_2 flow rate of 40 mL min^{-1} to determine the active pyrolytic zone by using Mettler Toledo, Switzerland; TGA 851^e/L F/1100 thermogravimetry analyzer.

Table 2
Physical properties of thermal and catalytic pyrolytic oils at the optimum condition.

		Viscosity (Pa s)	Calorific value (MJ kg^{-1})	pH	Water content (%)
Karanja pyrolytic oils	Thermal	0.051671	37.65	4.05	1.33
	8:1 CaO	0.019629	40.42	7.55	1.55
	8:1 Al_2O_3	0.02089	41.21	6.27	1.94
	8:1 Kaolin	0.02481	39.04	6.27	2.82
	Diesel	0.004575	45	–	–

2.3. Thermal and catalytic pyrolysis

Thermal pyrolysis experiments were carried out to determine the optimum temperature for maximum liquid yield. About 40 g of sundried Karanja seed powder was chosen as feed for all pyrolysis experiments. Thermal pyrolysis experiment was conducted using a stainless steel cylindrical semi batch reactor (Length:

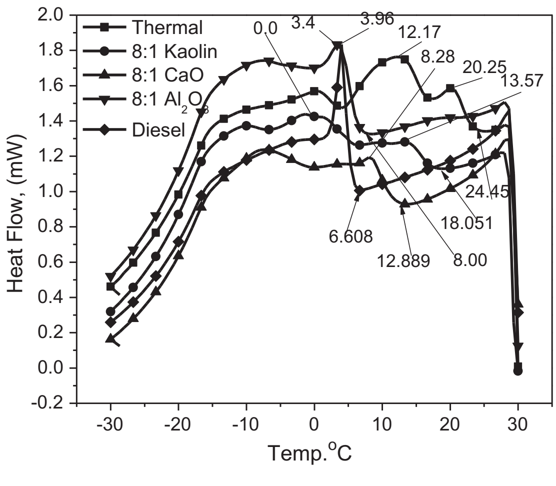

Fig. 5. DSC analysis of pyrolytic oils.

21 cm, ID: 6 cm) without any inert environment. The pyrolysis experiments were performed between 500 and 600 °C at 25 °C augmenting temperature. The reactor was filled with the required amount of powered Karanja seed and inserted vertically into the cylindrical furnace. The desired temperature for pyrolysis was controlled with the help of PID controller. The volatiles of Karanja seed generated during pyrolysis were condensed through a glass condenser by using freeze water as cooling media. The condensed liquid was collected, measured and used for further analysis. The remaining char present in the reactor was collected and weighed after cooling the reactor to room temperature. The percentage yield of pyrolytic oil, char and non-condensable volatiles were calculated on the basis of feed (Eqs. (1)–(3)).

$$\%\ \text{Liquid yield} = (\text{Liquid weight}/\text{Feed weight}) \times 100 \qquad (1)$$

$$\%\ \text{Char yield} = (\text{Char weight}/\text{Feed weight}) \times 100 \qquad (2)$$

$$\%\ \text{Gas yield} = 100 - (\%\text{Liquid yield} + \%\text{Char yield}) \qquad (3)$$

The optimum temperature for maximum liquid yield produced from Karanja seed thermal pyrolysis was decided on the basis of highest weight% yield of the pyrolytic oil.

Catalytic pyrolysis was carried out using the same reactor where a mixture of Karanja seed and catalyst was fed at the optimum temperature (550 °C). The experiments were carried out using three catalysts at different feed to catalyst ratios (2:1, 4:1 and 8:1). Aluminum oxide (Al_2O_3) and calcium oxide (CaO) were purchased from Loba Chemie. (P) Ltd., India and Kaolin were purchased from Central Drug house (P) Ltd., India. The catalysts were used directly without any pretreatment and the yield was calculated as described in Eqs. (1)–(3). The pyrolytic oil obtained from thermal and catalytic pyrolysis was compared on the basis of weight% yield, physical and chemical properties. Later on the process was optimized and the ratio of feed to catalyst for maximum production of pyrolytic oil was determined.

2.4. Characterization of pyrolytic liquid

The liquid produced from pyrolysis was separated into two fractions such as oil phase (top liquid) and the aqueous phase (bottom liquid). The oil phase was considered as fuel oil [5,6] and characterized on the basis of water content, functional groups present, cold flow properties and compositions. The rheology study was conducted with the help of rheometer (HAKEE Rheostress 1) using Cone (Meas. Cup Z 43 (Series 1)) and Plate (PP 35 Ti, D = 35 mm) type geometry. The rheological data were collected at 25 ± 0.05 °C at 50 rpm and the temperature was controlled accurately by HAAKE DC-50 temperature controller. A series of rheological data was collected and the average was taken as the viscosity of the oil.

The calorific value was determined using Bomb calorimeter followed by ASTM standard D 240 methods [23]. Karl Fischer water analyzer (Metrohm 787 KF Titrino) was used to determine the water content of pyrolytic oil. For accurate measurement of water content each experiment was repeated three times and the average value was taken into consideration. Eutech water proof (pH Spear) pH meter was used to determine the pH of the pyrolytic oil.

The cold flow properties of pyrolytic oil were studied by DSC analysis using METTLER TOLEDO DSC 1 star^e system analyzer [24]. The cold flow properties also can be termed as pour point. Pour point of a liquid is the temperature at which the liquid become semi solid and loses the flow ability. This is being done manually using ASTM D5949-10 standard method [25]. Pyrolytic oil obtained from the optimum conditions from both thermal and catalytic pyrolysis was selected to measure the cold flow property. For this 10 ± 0.05 mg of oil sample was taken in an aluminum crucible covered by a single perforated lead and DSC experiment was performed under N_2 flow rate of 50 mL min^{-1}. The pyrolytic oil was analyzed by cooling the sample from 30 °C to −30 °C and their respective heat flow profile was collected with respect to temperature.

Fourier transform infrared spectroscopy (FTIR) is a technique which provides information regarding functional groups present in the sample. DRS attached with Excalibur Bio-Rad spectrophotometer (Model FTS 3500 GX) FTIR analyzer was used for the same. The IR spectrum was collected within the range between 400 and 4000 cm^{-1} at a scan rate of 40 and at a step size of 4 cm^{-1}. Initially spectrum of the blank sample holder was measured and after that one drop of the liquid sample was dropped in the sample holder and their respective transmittance with respect to wave number was obtained.

GC–MS analysis was carried out to identify the composition of pyrolytic oil. Perkin Elmer Clarus 600/680 GC–MS analyzer was programmed at 40 °C for 0.5 min with the total GC run time of 30 min. The temperature was increased at the rate of 10 °C min^{-1} to 300 °C. Elite 5 MS column of diameter 0.250 μm, length 30 m was used. Exact 1 μL volume of sample was injected into the column with a carrier gas (Helium) flow rate of 0.6 mL min^{-1}. The GC chromatogram was collected at different retention time and the respective mass spectra were identified from the preinstalled NIST library.

3. Results and discussions

3.1. Characterization of Karanja seed

The proximate and ultimate analysis of the sun dried Karanja seed was carried out and presented in Table 1. The result confirmed that Karanja seed restrained maximum volatile matters (89.23%) with lower% of moisture (7.27), ash (1.5) and fixed carbon (2.0) contents. More volatile matter produces more liquid and gaseous fuel during pyrolysis. The ultimate analysis determined the presence of carbon (53.04%), oxygen (35.527), hydrogen (7.32%), nitrogen (3.94%) and sulfur (0.173%) in Karanja seed. Lower sulfur content in the raw materials makes them suitable feed for pyrolysis to produce good quality of liquid and gaseous fuel. The presence of volatiles determines the combustibility of biomass, the existence of extractives provides higher impact on the heating value as well as the yield of pyrolytic liquid [26]. The extractive content was determined by using hexane and ethanol as solvent in a Soxhlet apparatus. The result confirmed that maximum 53.19% of extractives were present in Karanja seed (Table 1). The presence of high extractive content indicated that it may produce a higher percentage of oil than gas and char during pyrolysis.

Karanja seed was characterized on the basis of thermal degradation temperature. The degradation temperature depends on the composition where cellulose, hemicelluloses and lignin play a vital role. The degradation profile was observed by TGA/DTG analysis and depicted in Fig. 1 which shows the TGA and DTG thermograph of Karanja seed with respect to temperature. It was found that Karanja seed pyrolysis followed step wise degradation with

Table 3
Minimum flow temperature of pyrolytic oils as determined by DSC analysis.

Oil	Peak temp. (°C)	Onset temp. (°C)
Diesel	3.96	6.6
Thermal	12.05	24.45
8:1 Al_2O_3	3.4	8.00
8:1 Kaolin	0.0	18.05
8:1 CaO	8.28	12.88

increase in temperature due to its composition. Normally thermal degradation is a function of composition such as celluloses, hemicelluloses, lignin and extractives [27–29]. Initially, moisture and more volatile compounds were removed within 160 °C and after that the thermal degradation of Karanja seed started and proceeded followed by two steps such as degradation of hemicellulose and cellulose. At higher temperature lignin degrades. Hemicelluloses degrade at lower temperature than cellulose which was noticed by the 2nd peak (166–353 °C) of the DTG thermograph. The 3rd peak observed in the range between 353 and 460 °C indicated the degradation of cellulose. At higher temperature lignin degrades slowly till the end stage of degradation. At the end of pyrolysis, residue of Karanja seed remained as char. It was observed that maximum degradation occurred during second and third stage in the temperature range between 160 and 460 °C. This temperature range was considered as active pyrolytic zone for Karanja seed where maximum volatization took place.

3.2. Thermal pyrolysis of Karanja seed and the effect of temperature on pyrolysis

Thermal pyrolysis of Karanja seed was performed in a semi batch reactor and the influence of temperature on product yield is shown in Fig. 2. The result revealed the influence of temperature with relation to weight % yield of liquid, char and non-condensable gases. It was confirmed that temperature had a positive affinity towards the yield of oil and non-condensable gas. The % of liquid yield increased up to 550 °C and subsequently decreased with increase in temperature (600 °C). This may be due the increase in the yield of non-condensable gases which was generated as a result of various secondary reactions occurred at elevated temperatures [30–33].

Literature reported that pyrolysis at elevated temperature produce more amount of H_2 and CO which results in less liquid yield. The release of gases may be due to the reduction reaction of char at high temperatures as follows:

$$C + CO_2 = 2CO - 172 : 58\ \text{kJ mol}^{-1} \qquad (4)$$

$$C + H_2O = CO + H_2 - 131 : 40\ \text{kJ mol}^{-1} \qquad (5)$$

Eqs. (4) and (5) are seems to be endothermic reactions which occur at high temperatures. With increase in the pyrolysis temperature over 550 °C, the secondary cracking or reforming reactions of the heavy-molecular-weight compounds in the pyrolysis vapors become active. This leads to the rapid decrease in the yield of bio-oil by significantly increasing the non-condensing gases such as H_2 and CO [34]. Hence, 550 °C was considered as the optimum temperature to produce maximum liquid yield of 55.17% with the formation of less non-condensable gas (25.09%) and 19.81% of char. It was noticed that the liquid produced by thermal pyrolysis of Karanja seed got separated into two phases as it condensed [6,7,33]. Mourant et al. (2013) reported that the presence of more extractives in biomass produce two categories of pyrolytic liquid which get separated into oil (organic) and aqueous (inorganic)

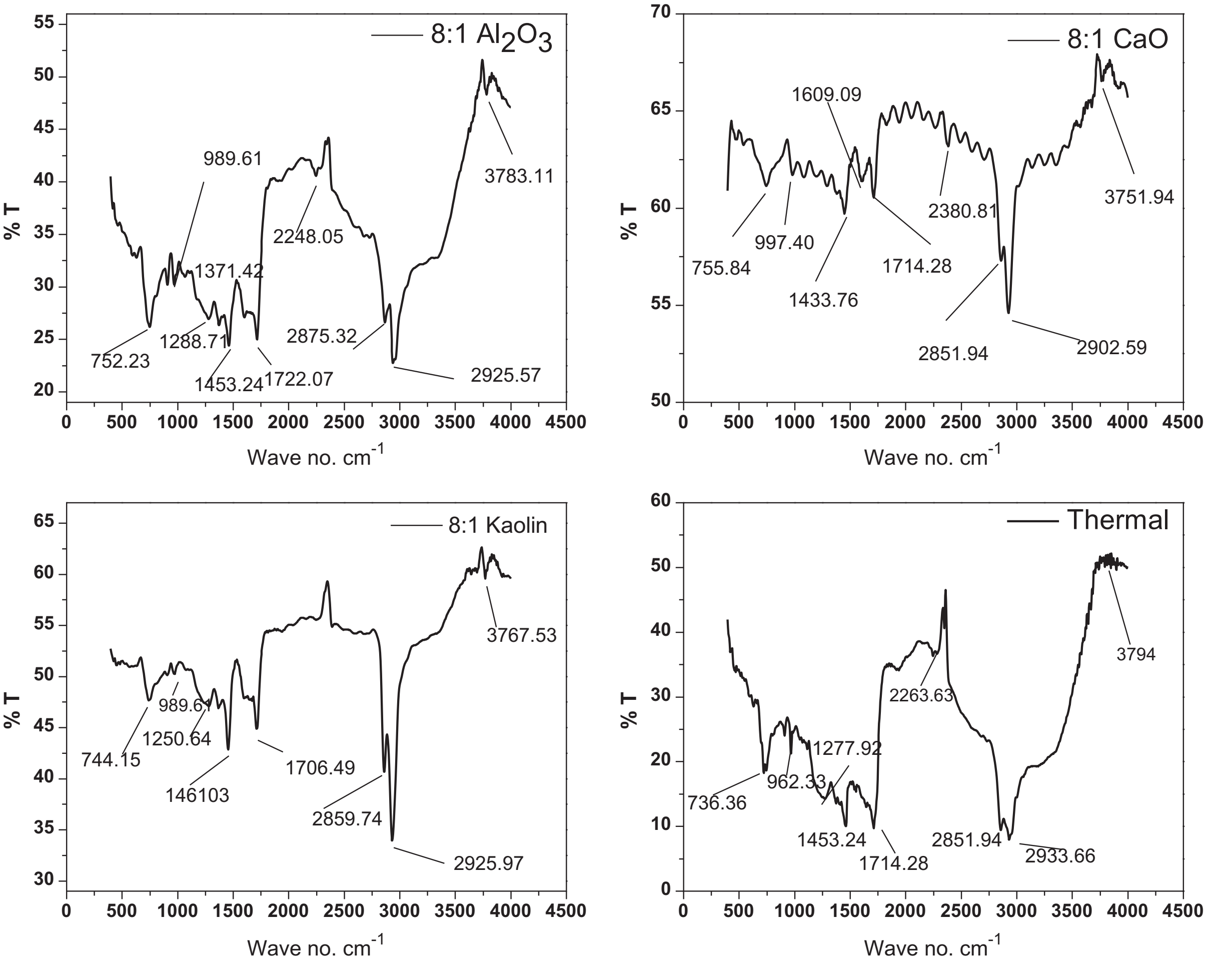

Fig. 6. FTIR analysis of pyrolytic oils.

phase [33]. The weight % yield of oil and aqueous liquid was calculated to be about 33% and 22.17% respectively (Fig. 3).

3.3. Effect of catalyst on pyrolytic liquid yield

Catalytic pyrolysis of Karanja seed was carried out at three different feed to catalyst ratio such as 2:1, 4:1, 8:1 at 550 °C. Fig. 4 demonstrates the effect of catalyst (a) CaO, (b) Al_2O_3 and (c) Kaolin on the yield of liquid at various feed to catalyst ratio. The yield of total liquid was high for CaO and Al_2O_3 at 4:1 catalyst ratio and Kaolin at 2:1 catalytic ratio. However, the yield of pyrolytic oil was completely dissimilar. Maximum yield of oil was observed for each catalyst (CaO, Al_2O_3 and Kaolin) at 8:1 Karanja seed to catalyst ratio. The yield of catalytic pyrolytic oil was 31.28%, 34.49% and 35.17% for CaO, Al_2O_3 and Kaolin respectively. This confirmed that yield of pyrolytic was higher at a lower feed to catalyst ratio. This further established that the pyrolytic liquid yield varies with type of catalyst and feed to catalyst ratio. The yield of aqueous yield was lower than the oil yield at 8:1 feed to catalyst ratio for each catalyst. The aqueous phase is rich in water and water soluble chemicals and it cannot be used as fuel. Since the main objective of the work was to produce liquid fuel, hence, the focus was only on the yield of pyrolytic oil. The comparison between thermal and catalytic pyrolysis confirmed that catalyst had an effect on the yield of liquid. The result showed that yield of the pyrolytic oil was less for CaO catalytic pyrolysis than thermal pyrolysis. However the yield was marginally higher (2–3%) for Al_2O_3 and Kaolin catalytic pyrolysis at 8:1 feed to catalyst ratio than thermal pyrolysis.

3.4. Effect of catalyst on physical properties of pyrolytic oil

Table 2 represents the physical properties of the thermal and catalytic pyrolytic oil produced at the optimum condition. The physical properties such as viscosity, pH, calorific value and water content were evaluated and compared. The decrease in viscosity of oil was observed for every catalytic pyrolysis over thermal pyrolysis. Catalytic pyrolysis with CaO at 8:1 ratio produced less viscous (0.019629 Pa s) pyrolytic oil than other catalytic pyrolysis. A variation in calorific value of the catalytic pyrolytic oil was noticed. The calorific value of thermal pyrolytic oil was found to be 37.65 MJ kg^{-1}. It was observed that the calorific value increased for all the three catalytic pyrolysis with CaO (40.42 MJ kg^{-1}), Al_2O_3 (41.21 MJ kg^{-1}) and Kaolin (39.04 MJ kg^{-1}) in comparison with thermal pyrolysis. The positive impact of catalytic pyrolysis on pH was also observed. All the three catalysts were competent to increase the pH resulting in less acidic oil and especially CaO helped in altering the pH from 4.05 to 7.55. From Table 2, it can be seen that the water content of all the catalytic pyrolytic oil increased slightly in comparison with thermal pyrolytic oil. Catalytic pyrolysis has resulted in the formation of more water, which may be the cause for increase in water content.

In general, oxygen content of thermal pyrolytic oil is higher which decreases the stability as well as the calorific value. The other factor that also affects the thermal stability is the pH of the oil. Lower pH increases the acidity of the pyrolytic oil which is thus not suitable as fuel for diesel engine. The major drawback of pyrolytic oil is higher viscosity which creates a problem during the atomization in a diesel engine. All these physical properties are related to each other. This can be overcome by catalytic pyrolysis. During catalytic pyrolysis, the oxygen is removed from pyrolysis vapor with the formation of CO_2, CO and H_2O. This results in increase in calorific value of pyrolytic oil. The formation of water decreases the viscosity of pyrolytic oil. Water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of pyrolytic oil in the engine [3,32–34].

3.5. DSC analysis of pyrolytic oil: effect of catalyst on cold flow property

The DSC curve of diesel and pyrolytic oil obtained from the optimum condition is presented in Fig. 5. DSC analysis was also used elsewhere to determine the cold flow properties of bio-diesel by cooling the samples that determine cloud point and pour point [24,25]. The cold flow properties of pyrolytic oil were compared with diesel which is depicted in this figure and the temperature related to the cold flow properties are presented in Table 3. From this study, it was observed that during cooling thermal pyrolytic oil and 8:1 Kaolin pyrolytic oil provided two crystallization peak points where only one crystallization peak point was observed from other pyrolytic oils and diesel. Two crystallization peak points indicated that both thermal and 8:1 Kaolin pyrolytic oil is a mixture of saturated and unsaturated fatty acid methyl esters where other catalytic pyrolytic oil contains only single compound. The first crystallization peak observed at the higher temperature region between 13 and 21 °C was due to the presence of saturated methyl esters of fatty acids. The lower temperature crystallization point is denoted by the second peak and observed in the range between

Table 4
Composition of thermal pyrolytic oil.

RT	Compound name	Area%	MW
Karanja thermal pyrolysis oil			
12.52	Phenol	0.537	94
12.73	Trans-2-Methyl-4-N-Butylthiane, S,S-Dioxide	0.795	204
12.85	Benzene, 1-Ethyl-3-Methyl-	0.468	120
13.95	Phenol, 2-Methyl-	0.551	108
14.28	Phenol, 4-Methyl-	0.551	108
14.49	Carbonic acid	0.579	258
14.69	1R,2C,3T,4T-Tetramethyl-cyclohexane	0.891	140
15.86	Phenol, 2-Ethyl-	0.548	122
15.91	1-Hexen-3-Yne, 2,5,5-Trimethyl-	0.895	122
16.24	Dodecane, 1-Fluoro-	0.589	188
16.66	Cyclododecene	0.685	166
16.83	Phenol, 3-(1-Methylethyl)-	0.782	136
17.64	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.440	218
17.74	Hentriacontane	0.456	436
18.20	2,2′-Bifuran	0.710	134
19.05	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.745	218
19.15	Hentriacontane	0.465	436
20.09	Methyl 12,15-Octadecadienoate	1.402	294
20.32	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.869	218
20.38	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.887	218
20.46	Hentriacontane	1.402	436
20.70	9-Octadecenamide, (Z)-	0.896	238
21.47	Bicyclo[4.1.0]Heptane, 7-Pentyl-	0.723	166
21.54	Chloroacetic Acid	0.723	290
21.62	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	1.151	218
21.69	Hexadecane	1.025	226
22.03	N-Methyldodecanamide	1.095	213
22.70	8-Heptadecene	5.310	238
22.79	8-Heptadecene	0.703	238
22.85	Hentriacontane	2.534	436
23.89	Chloroacetic Acid	0.840	290
23.95	Hentriacontane	0.675	436
24.99	8-Heptadecene	0.966	238
25.05	Hentriacontane	0.966	436
25.17	2-Pentacosanone	0.800	366
25.23	Hexadecanenitrile	3.018	237
25.35	Methyl 3,4-Di-O-Methyl-.Beta.-L-Arabinopyranoside	4.027	192
26.17	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.888	218
26.23	Hentriacontane	1.933	436
27.52	Hentriacontane	3.725	436
27.61	Oleanitrile	18.126	263
27.85	Octadecanenitrile	3.430	265
29.07	Hexadecanamide	1.810	255
29.58	N-Methyldodecanamide	1.283	213
29.99	I-Propyl 9-Octadecenoate	1.505	324
30.76	Hentriacontane	1.017	436

0 and 13 °C was due to the presence of unsaturated fatty acids and its methyl esters. The presence of acids and its methyl esters was also determined from the physical properties and FTIR analysis which support this discussion. However, for 8:1 Al_2O_3 and 8:1 CaO pyrolytic oil a single crystallization peak was observed with a lower peak temperature which was closer to diesel. The temperature at which nucleation growth starts is termed as onset crystallization temperature. The DSC analysis confirmed that 8:1 Al_2O_3 pyrolytic oil offered minimum nucleation temperature (8 °C) than other catalytic and thermal pyrolytic oil whereas diesel's minimum nucleation temperature is 6.6 °C. This result confirmed that catalytic pyrolysis improves the cold flow property of pyrolytic oil in such a way that the use of catalyst decreases the onset nucleation temperature of pyrolytic oil as well as the crystallization temperature in comparison with the thermal pyrolytic oil.

3.6. FTIR analysis of pyrolytic oil

The vibrational spectrum of a molecule is thought to be a unique physical property and characteristic of that molecule. FTIR analysis provides an infrared spectrum which can be used as a fingerprint for the identification of functional groups of unknown compounds. Each and every molecule or the functional groups attached to the molecule produce characteristic and reproducible absorption in the spectrum. This information helps to indicate whether the molecule is linear or branched chained aliphatic or aromatic compound. FTIR analysis of the pyrolytic oils was carried out and their respective spectra are presented in Fig. 6. Very similar FTIR spectra were obtained for Karanja seed thermal and 8:1 Al_2O_3, 8:1 Kaolin and 8:1 CaO catalytic pyrolytic oils. The presence of aryl groups were observed in the range of 735–770 cm^{-1} (especially aromatic C—H out of plane bending vibrations) and 950–1225 cm^{-1} (aromatic C—H in-plane bending vibrations). The alcohol group (primary or secondary OH in-plane bending vibrations) was identified in between 1260 and 1350 cm^{-1}. Saturated aliphatic group within 1370–1380 cm^{-1} and 1430–1470 cm^{-1} showed the presence of Methyl C—H asym./sym bending vibrations and Methylene C—H asymmetric./sym. stretch. Saturated aliphatic group compounds were similarly observed in between 2845–2865 cm^{-1} and 2915–2935 cm^{-1} for all pyrolytic oils. The carboxylic acid group in thermal pyrolysis oil was observed at 1700–1725 cm^{-1}; however this group was not identified for catalytic pyrolytic oils. Ketone group compounds were not present in thermal pyrolytic oil but observed in all catalytic pyrolytic oils within 1705–1725 cm^{-1}. Aliphatic cyanide/nitrile which is nitrogen multiples and cumulative double bond compounds were identified at 2240–2280 cm^{-1} in all pyrolytic oils except 8:1 Kaolin pyrolytic oil. A peak of saturated aliphatic group, Methyl C—H stretching vibration was observed for 8:1 Al_2O_3 catalytic pyrolytic oil at 2860–2880 cm^{-1} which was not identified in other pyrolytic oils. Wave No. 1461.03 cm^{-1} and 1250.54 cm^{-1} denotes the presence of C=C—C Aromatic ring stretching (aryl group) and aromatic primary amine, C—N stretch which was observed in 8:1 CaO and 8:1 Kaolin pyrolytic oil but not present in 8:1 Al_2O_3 and thermal pyrolytic oil. Water analysis confirmed that pyrolytic oil contains very less amount of water which was identified by FTIR analysis (OH group stretch) in the range of 3750–3795 cm^{-1}.

Table 5
Composition of 8:1 CaO catalytic pyrolytic oil.

RT	Compound name	Area%	MW
Karanja catalytic pyrolytic oil (8:1 CaO)			
12.74	Trans-2-Methyl-4-N-Butylthiane, S,S-Dioxide	0.486	204
14.28	Phenol, 4-Methyl-	0.806	108
14.49	Carbonic Acid, Methyl Tridecyl Ester	0.602	258
14.62	Dodecane, 1-Fluoro-	0.619	188
14.70	1r,2c,3t,4t-Tetramethyl-Cyclohexane	0.643	140
16.13	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.967	218
17.64	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.720	218
17.75	Hentriacontane	0.458	436
19.06	Chloroacetic Acid, Tetradecyl Ester	0.978	290
19.15	Hentriacontane	0.563	436
20.38	Chloroacetic Acid, Tetradecyl Ester	1.294	290
20.47	Hentriacontane	1.351	436
21.47	Bicyclo[4.1.0]Heptane, 7-Pentyl-	0.933	166
21.63	8-Heptadecene	2.114	238
21.70	Hentriacontane	1.407	436
22.8	8-Heptadecene	2.918	238
22.86	Hentriacontane	1.999	436
23.90	Chloroacetic Acid, Tetradecyl Ester	0.874	290
23.96	Hentriacontane	0.922	436
25.06	Octadecane, 2,6,10,14-Tetramethyl-	0.977	410
25.18	2-Pentacosanone	5.306	366
25.24	Hexadecanenitrile	1.973	237
25.36	Tetradecanoic Acid, 10,13-Dimethyl-, Methyl Ester	1.111	270
26.18	Hexacosanol, Acetate	0.904	426
26.23	Hentriacontane	0.576	436
26.32	Octadecan-4-One	0.960	268
27.48	Z,Z-6,27-Hexatriactontadien-2-One	14.936	516
27.62	Oleanitrile	7.185	263
27.74	2-Pentacosanone	3.780	366
27.85	Octadecanenitrile	2.095	265
29.19	3-Hexadecanone	1.451	240
29.59	N-Methyldodecanamide	0.690	213

Table 6
Composition of 8:1 Al_2O_3 catalytic pyrolytic oil.

RT	Compound name	Area%	MW
Karanja catalytic pyrolytic oil (8:1 Al_2O_3)			
12.5	Phenol	0.752	94
12.87	Benzene, (1,3,3-Trimethylnonyl)-	0.963	246
12.725	Trans-2-Methyl-4-N-Butylthiane, S,S-Dioxide	0.559	204
13.936	Phenol, 2-Methyl-	0.837	108
14.48	Carbonic Acid, Methyl Tridecyl Ester	0.536	258
14.62	Dodecane, 1-Fluoro-	0.437	118
14.68	1r,2c,3t,4t-Tetramethyl-Cyclohexane	0.454	140
14.266	Phenol, 4-Methyl-	0.357	108
16.11	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.357	218
16.23	Dodecane, 1-Fluoro-	0.674	118
17.63	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.555	204
17.73	Hentriacontane	0.372	436
18.19	2,2′-Bifuran	0.625	134
19.04	Chloroacetic Acid, Tetradecyl Ester	1.018	290
19.14	Hentriacontane	0.590	436
20.37	Chloroacetic Acid, Tetradecyl Ester	1.071	290
20.46	Hentriacontane	1.378	436
21.46	Bicyclo[4.1.0]Heptane, 7-Pentyl	0.768	166
21.62	8-Heptadecene	1.295	238
21.69	Hentriacontane	1.048	346
22.68	8-Heptadecene	0.610	238
22.71	8-Heptadecene	3.655	238
22.79	8-Heptadecene	0.837	238
22.86	Hentriacontane	2.043	436
23.91	Chloroacetic Acid, Tetradecyl Ester	0.729	290
23.97	Hentriacontane	0.787	436
24.71	Methyl 6,9-Octadecadienoate	5.878	294
25.07	Hentriacontane	0.822	436
25.19	2-Pentacosanone	3.004	366
25.25	Hexadecanenitrile	2.267	237
25.37	Methyl 11-Methyl-Dodecanoate	1.166	228
26.20	1r,2c,3t,4t-Tetramethyl-Cyclohexane	1.086	140
26.25	Hentriacontane	0.925	436
26.33	Octadecan-4-One	0.432	268
27.64	Oleanitrile	11.842	263
27.77	2-Pentacosanone	4.739	366
27.88	Octadecanenitrile	3.167	265
29.09	Hexadecanamide	1.432	255
29.63	N-Methyldodecanamide	0.765	213
30.84	Hentriacontane	1.258	346

Table 7
Composition of 8:1 Kaolin catalytic pyrolytic Oil.

RT	Compound name	Area%	MW
Karanja catalytic pyrolytic oil (8:1 Kaolin)			
10.86	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.441	218
12.74	Trans-2-Methyl-4-N-Butylthiane, S,S-Dioxide	0.441	204
14.49	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.711	218
14.25	Dodecane, 1-Fluoro-	0.569	118
14.69	1r,2c,3t,4t-Tetramethyl-Cyclohexane	0.609	140
16.12	Trans-2-Methyl-4-N-Butylthiane, S,S-Dioxide	0.670	204
16.23	Dodecane, 1-Fluoro-	0.367	118
17.64	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	0.825	218
17.74	Dodecane, 1-Fluoro-	0.603	118
19.05	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	1.872	118
19.14	Hentriacontane	1.005	436
20.38	Chloroacetic Acid, Tetradecyl Ester	1.646	290
20.46	Hentriacontane	0.810	436
21.62	Trans-2-Methyl-4-N-Pentylthiane, S,S-Dioxide	2.779	218
21.69	Hentriacontane	1.405	436
22.79	8-Heptadecene	3.597	238
22.86	Hentriacontane	4.341	436
25.18	2-Pentacosanone	7.824	366
25.24	Hexadecanenitrile	3.047	237
25.35	Tetradecanoic Acid, 10,13-Dimethyl-, Methyl Ester	1.146	270
25.84	L-(+)-Ascorbic Acid 2,6-Dihexadecanoate	3.311	652
26.31	Octadecan-4-One	0.992	268
27.48	Z,Z-6,27-Hexatriactontadien-2-One	6.580	516
27.61	Oleanitrile	4.804	236
27.74	2-Pentacosanone	6.648	366
27.86	Octadecanenitrile	4.202	265
29.09	Hexadecanamide	1.187	255
29.18	Octadecan-4-One	1.014	268
29.59	N-Methyldodecanamide	0.338	213

3.7. GC–MS analysis of pyrolytic oil

The composition analysis of thermal and catalytic pyrolytic oils obtained at the optimum condition was determined by GC–MS analysis and presented in Tables 4–7. Pyrolytic oil is a complex mixture of several oxygenated compounds. These compounds involve phenol, acids, esters, hexane, levoglucosan, amide, nitrile, benzene, furan and other alkane compounds. The effect of catalyst on thermal pyrolysis was observed and discussed.

It was observed that similar kinds of compounds were present in thermal and catalytic pyrolytic oil with a little variation. Acetic acid and carbonic acid were present in thermal pyrolytic oil; however the ester forms of such acids were identified in all catalytic pyrolytic oils. It was thus confirmed that catalyst converts the acids to esters and as a result the pH of pyrolytic oils changed. The presence of phenol was detected in thermal, 8:1 CaO and 8:1 Al_2O_3 catalytic pyrolytic oil, whereas no such compound was identified in 8:1 Kaolin pyrolytic oil. Both thermal and 8:1 Al_2O_3 catalytic pyrolysis produced bi-furan compounds, which were not present in other catalytic pyrolytic oils. The GC–MS analysis confirmed that Karanja thermal and catalytic pyrolytic oil contains a maximum amount of hentriacontane, 8-heptadecene, oleanitrile, z,z-6, 27-hexatriactontadien-2-one, trans-2-methyl-4-n-pentylthiane,s,s-dioxide and glucosan compounds with a lower amount of benzene, acids and other compounds.

The decomposition of cellulose produces levoglucosan, furfural, hydroxymethyl furfural and alcohol while hemicellulose decomposition does not yield significant amounts of levoglucosan. The acetic acid produced during pyrolysis could be due to the deacetylation of the hemicelluloses. Acetic acid and levoglucosan is the major product produced from the pyrolysis of cellulose. The formation of levoglucosan is attributed to chain-end depolymerization reaction of cellulose while β-scission reactions inside the polymer chain and successive molecular and radical reactions are responsible for the formation of acetic acid [26]. Levoglucosan, levoglucosenone, furfural, substituted furans, and smaller chemicals (e.g., substituted aldehyde and ketones) were derived from cellulose pyrolysis [35]. Decomposition of lignin resulted in many low molecular weight chemical compounds. In general, lignin contains aromatic rings attached with hydroxyl and methoxyl groups, which can be converted to benzene, phenols, cresols, and substituted phenols. The alkylephenols and liquid monoaromatics are further hydrodealkylated to produce phenol and benzene. The existence of extractives catalyzes the formation of acidic compounds such as acetic acid and levoglucosan while its absence enhances the formation of CO_2 and water. Extractive produces more organic compounds such as methanol, methane, and aldehyde. Methoxyl group in lignin units is the most important precursor of methanol; while the dissociation of methoxyl and methylene groups is crucial for methane formation [26].

4. Conclusion

Karanja seed is one of the renewable sources which can be cultivated worldwide and utilized as a potential feed stock for pyrolysis. Both thermal and catalytic pyrolysis of Karanja seed was carried out and the resultant oils were characterized for their physical properties. Thermal pyrolysis was carried out in a semi batch reactor and it was found that 550 °C was the optimum temperature for maximum yield of the pyrolytic liquid. Catalytic pyrolysis was carried out at this temperature using three different catalysts such as CaO, Al_2O_3 and Kaolin in three different feed to catalyst ratio. The catalytic effect of Al_2O_3 and Kaolin on pyrolysis was evident from the fact that these two catalysts marginally increased the yield of pyrolytic liquid in comparison with thermal pyrolysis. On the other hand, such positive result was not observed for CaO catalyst. The yield of catalytic pyrolytic oil was maximum 31.28%, 34.49% and 35.17% for CaO, Al_2O_3 and Kaolin respectively at the ratio of 8:1. Hence, 8:1 feed to catalyst ratio was accepted as the optimum condition for maximum yield of pyrolytic oil from Karanja seed. However thermal pyrolytic yield of oil was about 33% by weight. The comparison between thermal and catalytic pyrolysis confirmed that catalyst had a little effect on the yield of pyrolytic oil. However, all the three catalysts resulted in better oil quality in terms of enhanced calorific value, reduced viscosity and changed pH. The composition study signified that the acids produced during thermal pyrolysis were converted to their esters during catalytic pyrolysis. The results thus confirmed that CaO, Al_2O_3 and Kaolin can be used as a catalyst to produce better quality of pyrolytic oil from Karanja seed. On the basis of yield and calorific value, the Kaolin and Al_2O_3 are the better catalysts compared to CaO. The pyrolysis study concluded that Karanja seed pyrolytic oil can be used as alternative fuel in a diesel engine or for the production of bio-chemicals.

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